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Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery

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ABSTRACT

This paper presents the essential features of an efficient and environmentally attractive pyrolysis for used tyres valorisation with energy and material recovery. The problem of tyres management strongly affects not only the environmental protection but even the resources maintenance, since problems related to the depletion of resources, energy demand and waste management, are strictly connected and required an integrated approach. A general guideline for EU member states, aims to reach a zero post-consumer amount of tyre disposal in landfills before the end of 21st century, to optimize and expand the already well studied ways of their treatment and find new ones, in order to accomplish a balance between economy and environmental protection. In this context, thermal treatment of end of life tyres could play a relevant role for the recovery of resources (matter and/or energy). During the past 10–15 years, several fundamental and applied studies showed that if carefully controlled, tyre pyrolysis can produce a number of valuable products. The final destination of the pyrolysis solid residue largely influences the industrial applications of pyrolysis.

Contents

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1. Introduction

Rapid social, economic, environmental and technological changes brought human society in front of unprecedented challenges and the need for waste valorization. Among other wastes related with the increase of economic level of societies, end of life tyres (ELTs) consist a continuously growing environmental problem with impacts to economy and health matters concerning every modern society. Additionally, end of life tyres consist a high calorific waste and thus it can be used in dedicated energy-to-waste plants as fuel substitute; and as feedstock to alternative thermochemical conversion plants for both energy and carbon material production. Apart from energy and carbon material production, a wide range of materials such as steel, fibers, shredders, oils, carbon filler could be also recovered, since they are the key components of the raw material, end of life tyres.

By examining the last decade's evolution on ELTs management in EU, it can be noticed that ELTs are treated by different ways and processes to material recovery, under regulatory or industrial specifications. Several ways of mechanical processing are used, such as retreading and reuse (up to 20% of the rejected tyres per year). Incineration or use of ELTs as alternative fuel was also applied. Since 1996, more than 24 million tons of ELTs have been recovered either through energy or material recovery. This has led to a considerable decline in land filling over time; a phenomenon which has been accelerated since 2000 and further, by implementing of the Landfill Directive which is due to the proactive industry initiative of establishing national Producer Responsibility schemes. As a result, only 4% of the end of life tyres are tipped today in landfills or have unknown recovery routes while recycling, recovery, reuse and retreading now contribute to a substantial 96% of end of life tyres recovery [1].

The use of tyre rubber granulate and powder is the main material recovery route (80%), followed by civil engineering applications and public works (18%), dock fenders, blasting mats ($<2\%$) and steel mills and foundries ($<1\%$). As for energy recovery, the main user of ELTs shreds or whole tyres remains the cement industry (92% in volume) [1]. Nevertheless, in the last decade, tyre industry, dealers and ELTs operators have substantially improved ELTs utilization. Europe has built up a complete framework of 3 types of ELTs management schemes, tax model (very limited though), free market and producer responsibility models [2].

As a method of thermochemical conversion, pyrolysis offers another new alternative route for high temperature resource recovery from tyres with energy optimization. Pyrolysis involves the thermal decomposition of a tyre or tyre shreds into low molecular weight products under an inert atmosphere. Pyrolysis products have historically yielded poor returns as the prices obtained for products failed to justify process costs [3]. Looking to the future among other researchers, Zabaniotou et al. [4] proposed a scheme for processing scrap tyres into higher added value carbon products such as activated carbon to be used in water purification. The research continued and showed that activated carbon from used tyres can adsorb pesticides from water in rural areas. In the proposed process, char is upgraded in a closed-loop activation step. The aim of this study was to conduct a survey on the current practices on energy and material recovery from end of life tyres and especially by pyrolysis for the production of gas, liquid and solid products in European Union and worldwide, as well as to undertake an overview of the legal and policy framework for pyrolysis including the possible uses of the product. Assessments of the environmental impacts and of the economic aspects, as well as a review of alternative outlets of the ELTs waste streams, are also presented. The final target was to describe and analyze the technical and economical viability features of pyrolysis as an efficient, eco-friendly and cost effective solution in ELTs management.

2. Policy and legislative issues

Due to the fact that used tyres demand special treatment under a prudent, integrated and environment-friendly (sustainable) way of managing, the European Union has elaborated many specific Regulations and Directives, in order to achieve these goals. Through this way, the preferred way of ELTs management to each Member State is bounded with better monitoring and control.

The main EU legislative acts are presented below:

- **Directive 75/442/EEC on waste management:** according to this directive, end-of-life tyres are classified as non-hazardous waste [5].
- **Directive 91/156/EEC**, through which various provisions of the previous directive were modified [6].
- **Regulation 259/93/EEC** for the monitoring–supervision and control of the trans-border shipment-transportation of waste [7].
- **Directive 1999/31/EU** about waste disposition and land filling. According to this, land filling of whole and shredded waste tyres is prohibited since July 2003 and July 2006, respectively [8].
- **Formation of the European Waste List 2000/532/EU:** waste tyres are sorted with the code «16 01 03», which means that they are not classified as hazardous waste [9].
- **Directive 2000/53/EU for the end of life vehicles:** this directive indicates that it is obligatory for tyres to be disassembled–dismantled from each end of life vehicle [10].
- **Directive 2000/76/EU for the incineration of waste:** this directive indicates the maximum acceptable emission standards for the cement industries which use waste tyres as an alternative energy source-fuel, starting in 2002. From December 2008, new provisions apply to cement kilns co-incinerating waste including end-of-life tyres. The cement kilns currently

Nomeclature

PCT	Passenger car tyres
PCTO	Passenger car tyre oil from pyrolysis
TT	Truck tyres
TTO	Truck tyre oil from pyrolysis
n.m.	not mentioned
b.d.	by difference
PAH	Polycyclic aromatic hydrocarbon
PASH	Polycyclic aromatic sulphur-containing hydrocarbons
A	preexponential factor (1 min^{-1})
A_i	preexponential factor for component i (1 min^{-1})
$E_{a,i}$	activation energy for reaction of component I (J/mol)
m	mass of component i of the tire (mg)
m_o	initial mass of component i (mg)
$m\infty$	mass of component i of the tire (mg) with nth order reaction rate.
N	total number of components evolving independently
r	reaction rate
C	mass concentration of the reactant
X	normalized mass fraction of the tire sample that has decomposed
k	rate constant
R	molar gas constant (8.314 J/mol/K)
T	temperature (K)
$T(t)$	temperature of component at time t (K)
$T(0)$	initial temperature (K)
t	time of reaction (min)

burning ELTs in Europe are already complying with this Directive [11].

- **COM (2003) 572: towards a thematic strategy on the Sustainable use of natural resources:** this document focuses on material recycling. Furthermore it states the Commission's goal of becoming a recycling society as a mean of reducing reliance upon natural resources and substituting secondary materials [12].
- **COM (2005) 666 final: European thematic strategy on prevention and recycling of waste provides** a holistic analysis of the major achievements in the waste management area for the past 30 years. It stresses a need to further developing approaches for the determination of best environmental options and for the setting of targets for recycling and recovery of waste, taking into account the differences between products and materials. Finally, it encourages the principle of producer responsibility, a strategy which is proactively applied by the tyre manufacturers since late 90's in anticipation of the European Union regulatory requirements [13].
- **COM (2005) 670 Thematic strategy on the sustainable use of natural resources (Annexes, IA):** this report reaffirms the five-step management hierarchy [14].
- **Regulation (EC) 1013/2006 Revisions on the shipments of waste:** this regulation sets requirements for the notification of waste transports were strengthened, requiring complete notifications of wastes within the EU including tyres [15].
- **REACH Regulation (EC) 1907/2006 and Directive 2006/121/EC adapting 67/548 EEC to REACH (Regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals)** applied to all chemicals, making industry bear responsibility to manage the risks posed by chemicals and provides appropriate safety information to their users. It requires the registration of substances including those that have been recycled, including tyres and granulates, etc [16].
- **Revised waste framework directive 2008/98/EC:** this directive sets the basic concepts and definitions related to waste management and lays down waste management principles such as the "polluter pays principle" or the "waste management hierarchy". It also introduces the concept of end of waste, by which selected waste streams could cease to be considered as waste if they comply with end of waste criteria. As it is considered from the legislative acts presentation, the European Union demonstrates a really strong determination in order to implement a holistic waste tyres' management planning. Through these acts, strict goals and standards are defined, as well as detailed obligations are imposed to each Member State [17].
- **COM (2011) 681: Communication from the commission to the European Parliament, the Council, The European Economic and Social Committee and the Committee of Regions**, states that "enterprises should have in place a process to integrate social, environmental, ethical and human rights concerns into their business operations and core strategy in close collaboration with their stakeholders", to fully meet their social responsibility [18].

A barrier in tyres pyrolysis application is related to the unclear process definition in the legislation. In EU, which legislation is a guide for every EU member, depolymerisation of tyres by gasification or pyrolysis, is an activity classified as incineration; Incineration plant is any stationary or mobile technical unit and equipment dedicated to the thermal treatment of wastes with or without recovery of the combustion heat generated. However, pyrolysis is not incineration but an energy and material recovery process and should be differentiate from incineration in order to be socially acceptable.

Pyrolysis of ELTs is an alternative, efficient and environmental valorisation process, rather than combustion–incineration which primarily is characterized as a destructive one. The existing lack in environmental standards and Best Available Techniques across Europe can be fulfilled by the existing environmental restrictions on waste incineration, since the expected pollutants from ELTs pyrolysis will contain no dioxins or furans (oxygen is absent from pyrolysis process in contrast to incineration units).

In addition, a closer collaboration between the Joint Alternative Management System of each country and the local scientific community should be promoted, in order to develop innovative valorisation techniques for ELTs. Following the basic principles of the Producer's Responsibility system, the established fees for the ELTs alternative management are gradually expected to be eliminated by further developing more profitable applications, thus gaining substantial economic benefits for the consumers. By the time JAMS play an even drastic role in financing new valorisation techniques instead of promoting their use only in contracting facilities, progress towards to that direction can be achieved. Following this approach, ELTs will be removed from the list of wastes needed to be destroyed—eliminated, and will be used as a valuable raw material, been the major mission of ETRMA as well [1].

The challenges affecting waste management companies are summed to the innovation of new products and services that are beneficial to society and enterprises themselves, while at the same time they minimize and prevent negative impacts. Most companies show intense interest in incorporating "social responsibility" in their activities, since they expect an increase in their profits in return. Moreover, they thus realize that applying secure operation in a stable environment, can sedate up to a certain extent, public's scepticism.

This can promote pyrolysis economics, since the effective use of the final products will be further improved by effective standardization to meet marketable specifications. As a result, all pyrolysis products can be effectively promoted and sold in local or neighbouring markets disciplining at the same time to the legal and policy framework of European Union.

3. Characteristics of end of life tyres

Tyres are produced by more than 100 different species [19]. The composition of different tyre parts like the tyre sidewall or the tyre tread varies due to the different desired characteristics of product.

The most common rubbers used for tyres are natural rubber (NR), styrene–butadiene rubber (SBR) and butadiene rubber (BR). The rubbers mostly consist of blends of two or three rubbers together with tyre additives. Because of these complex mixtures, the pyrolysis of tyres seems to be a complicated process involving a large number of chemical reactions and complex interactions of the single components. The rubbers referred to above, carbon black along with other addititives, are the main constituents of tyre. Natural rubber (NR), also called Indian Rubber or caoutchouc, is an elastomer (an elastic hydrocarbon polymer) that was originally derived from latex, a milky colloid produced by some plants. Styrene–butadiene rubber (SBR) is one of the most

Table 1
Used tyre characteristics.

Type of tyre	PCT	PCT	PCT	PCT	PCT	PCT	BT	PCT	PCT	TT	Rubber	Shred	
Composition (wt%)													
NR	–	–	–	30	29.59	–	–	–	–	–	–	–	
SBR	62.1	–	62.1	30	29.59	–	–	–	–	–	–	–	
NR+SBR	62.1	57.8	62.1	60	59.18	50	–	–	–	–	–	–	
Carbon black	31.0	23.1	31.0	30	29.59	25	–	–	–	–	–	–	
Extender oils	1.9	–	1.9	–	–	–	–	–	–	–	–	–	
Zinc oxide	1.9	–	1.9	10	2.96	1	–	–	–	–	–	–	
Stearic acid	1.2	–	1.2	–	0.59	–	–	–	–	–	–	–	
Sulphur	1.1	–	1.1	–	0.89	1	–	–	–	–	–	–	
Accelerator	0.7	–	0.7	–	–	–	–	–	–	–	–	–	
Steel	–	15.1	–	–	–	10	–	–	–	–	–	–	
Others	–	3.6	–	–	B.d.	B.d.	–	–	–	–	–	–	
GCV, MJ/kg	40	40	40	–	–	–	28.75	40	30.5	33.4	–	37.3	
Ultimate analysis (wt%)													
C	85.9	–	–	82.5	–	–	74.5	86.4	74.3	83.2	82.6	89.5	
H	8.0	–	–	6.4	–	–	6.5	8	7.2	7.7	7.3	7.3	
O	2.3	–	–	5.7	–	–	16.42	3.4	15.89	6.16	–	0.8	
N	0.4	–	–	0.5	–	–	0.95	0.5	0.9	1.5	0.7	0.3	
S	1.0	–	–	1.1	–	–	1.63	1.7	1.71	1.44	1.7	1.9	
Cl	–	–	–	–	–	–	–	–	–	–	–	0.04	
Ash	2.4	–	–	3.8	–	–	–	2.4	–	–	–	–	
Proximate analysis (wt%)													
Volatiles	66.5	62.2	–	–	–	–	55.2	62.2	58.2	66.1	66	69.1	
Fixed carbon	30.3	29.4	–	–	–	–	22.3	29.4	21.3	27.5	B.d	B.d.	
Ash	2.4	7.1	–	–	–	–	21	7.1	18.9	5	3.7	7.1	
Moisture	0.8	1.3	–	–	–	–	1.5	1.3	1.6	1.4	B.d.	1.1	
Reference	[21,22]	[23]	[24]	[25]	[26]	[19]	[27]	[28]	[29]	[29]	[30]	[31]	
Type of tyre	**PCT**	**PCT**	**PCT**	**PCT**	**PCT**	**PCT**	**PCT**	**PCT**	**SBR**	**TT**	**Shred**	**Pine wood**	**Rapeseed**
Composition (wt%)													
NR	–	–	–	–	–	–	–	–	–	–	–	–	–
SBR	–	–	–	–	–	–	–	–	–	–	–	–	–
NR+SBR	–	–	–	–	–	–	–	–	–	–	–	–	–
Carbon black	–	–	–	–	–	–	–	–	–	–	–	–	–
Extender oils	–	–	–	–	–	–	–	–	–	–	–	–	–
Zinc oxide	–	–	–	–	–	–	–	–	–	–	–	–	–
Stearic acid	–	–	–	–	–	–	–	–	–	–	–	–	–
Sulphur	–	–	–	–	–	–	–	–	–	–	–	–	–
Accelerator	–	–	–	–	–	–	–	–	–	–	–	–	–
Steel	–	–	–	–	–	–	–	–	–	–	–	–	–
Others	–	–	–	–	–	–	–	–	–	–	–	–	–
GCV, MJ/kg	–	36	27.37	36.74	38.3	–	–	–	–	–	38.6	18.2	23.4
Ultimate analysis (wt%)													
C	79.1	77.6	67.08	87.6	86	–	84.3	81.64	80.6	82	83.92	48.14	–
H	6.7	7	6.12	7.6	8.4	–	7.6	8.41	6.7	7.2	6.83	6.12	–
O	12	7.7	24.58	3.1	3.2	–	5.7	0.81	0.5	–	–	45.48	–
N	0.6	0.43	0.17	0.3	0.5	–	0.5	0.37	0	0.4	0.78	0.12	–
S	2.3	1.4	2.05	2.01	1.9	–	1.9	1.95	1.2	2.3	0.92	0.14	–
Cl	–	–	–	–	–	–	–	–	–	–	–	–	–
Ash	–	–	–	–	–	–	3.8	6.82	11.1	–	–	–	–
Proximate analysis (wt%)													
Volatiles	61.8	71.5	59.69	63	66	63.8 ± 2.5	–	–	–	–	64.97	69.08	79.44
Fixed carbon	28.9	28.5	19.45	–	29.1	32.5 ± 0.25	–	–	–	–	30.08	19.87	8.34
Ash	8.6	8.3	19.13	9.3	4.9	2.85 ± 0.25	–	–	–	–	4.16	10.0	4.56
Moisture	0.8	0.2	1.72	–	0	1.05 ± 0.1	–	–	–	–	0.75	1.05	–
Reference	[32]	[33]	[34]	[35]	[36]	[37]	[38]	[39]	[40]	[41]	[42]	[43]	[44]

versatile copolymer rubber compounds. It consists of the organic compound styrene and the chemical butadiene, with the amount of butadiene usually being about three times more than the amount of styrene. SBR is a stable synthetic rubber that is resistant to abrasion. Carbon black is virtually pure elemental carbon in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions [20].

Comparing published data, it seems that all passenger car tyres (PCT) have almost identical characteristics (Table 1). This is also true for truck tyres (TT) and bicycle tyres (BCT). However, there is a noticeable difference between PCT, TT and BCT characteristics due to their different manufacturing process. Ash content on BCT waste is comparable to TT and PCT. Oxygen content on bicycle tyre waste is low. Due to the larger amount of inorganics on tyres, BCT has lower GCV than TT and PCT [27].

In order to determine feedstock characteristics, analyses suitable for solid materials characterization are used such as proximate and elemental analyses. Proximate analysis separates the products into four groups: (1) moisture, (2) volatile matter, consisting of gases and vapors driven off during pyrolysis, (3) fixed carbon, the nonvolatile fraction of coal, and (4) ash, the inorganic residue remaining after combustion. Proximate analysis can also determine Btu values and sulphur content. Taking into consideration the proximate analysis, calculation of Gross Calorific value can be achieved.

A complementary method to proximate is the ultimate analysis. Its scope is the determination of the carbon and hydrogen in material, as found in gaseous products of feedstock's complete combustion, determining also the content of sulphur, nitrogen, and ash in the material as a whole, and oxygen content by difference. The carbon determination includes carbon been present in organic material and any other originally present as mineral carbonate. The hydrogen determination includes hydrogen in organic materials and in water associated with the organic feedstock. Nitrogen and sulphur are also present in tyres. Nitrogen quantity is assumed to be part of the organic material. As for sulphur, it is assumed to appear in three forms in organic material: as organic sulphur compounds; as inorganic sulphides, which are mostly appeared as iron sulphide pyrite and marcasite, and as inorganic sulfates. Tyre feedstocks are compared by their proximate and ultimate analysis. More analytically, elemental and ultimate analysis of various end of life tyres are presented in Table 1. Furthermore, characteristics of conventional biofuels are also added to Table 1, presenting substantial differences especially in GCV values.

4. Process of pyrolysis

Pyrolysis is the thermal decomposition of organic materials in the absence of oxygen, cracking them down to simpler organic compounds. It relies on the addition of heat to break chemical bonds, providing a mechanism by which organics decompose and vaporize. Most tyre pyrolysis processes operate within a temperature range of 250–500 °C, although some processes are reported to operate at up to 900 °C. At temperatures above approximately 250 °C, shredded tyres release higher amounts of liquid oil products and gases, while above 400 °C, the yield of oil and solid tyre-derived char may decrease relatively to gas production.

Pyrolysis can be classified as atmospheric, vacuum, catalytic, fast or slow according to the operation parameters applied. According to pressure applied, pyrolysis can be atmospheric or vacuum. The interest of vacuum pyrolysis [45] lies in the advantages associated with the decrease in the inert gas flow rate and residence time of volatiles in the reactor: lower energy requirements for the process; simpler devices for volatile product condensation; higher liquid yield and better control of its composition, either for increasing the yield of high value added components, such as dl-limonene [46] or for improving its fuel quality and better quality of the carbon black. Since the undesired

Table 2
Yields of products from pyrolysis laboratory scale.

Reactor type	Temp/re (°C)	Medium flow	Residence time	Catalysts	Yields: Gas (wt%)	Oil (wt%)	Char (wt%)	Reference
Rotary kiln	550	He, 200 ml/min	30 min	–	67	–	33	[3]
Fixed bed	400–460	N_2, 0.2–0.5 m^3/h	n.m.	–	2.8–17	36–62	31.6–51	[58]
Fixed bed	700	N_2	5 min	–	n.m.	n.m.	36	[59]
Fixed bed	1000	He	120 min	–	n.m.	n.m.	n.m.	[60]
Fixed bed	300–700	N_2, 1 dm^3/min	30 min	–	7.6–19	4.8–38.5	44–84	[61]
Fixed bed	1000	N_2, 200 ml/min	1 min	–	–	–	–	[73]
Fixed bed	550–800	N_2, 25 ml/min	60 min	–	7.4–7.8	47.2–48.4	41.5–42	[29]
Fixed bed	550–800	N_2, 25 ml/min	60 min	–	7.6–8.8	55.1–56	33.2–33.8	[29]
Fixed bed	500	N_2, 30 ml/min	30 min	–	16–25	35–44	39–40	[62]
Fixed bed	425–610	N_2, 6.5 l/min	n.m.	–	1–3.5	25–31	32–33	[25]
Fixed bed	500	N_2, 300 ml/min	150 min	–	n.m.	n.m.	n.m.	[63]
Fixed bed	350–550	He, 200 ml/min	15 min	–	20–29	30–38	33–50	[67]
Fixed bed	350–450	N_2	5–30 min	–	4	54	42	[64]
Fixed bed	720	N_2	120 min	–	n.m.	n.m.	n.m.	[21]
Fixed bed	570	N_2 1.5 l/min	60 min	–	4.3	57.1	38.7	[68]
Fixed bed	300–720	N_2 0.11 L/min	120 min	–	2.4–14.8	3.6–58.8	26.4–94	[54]
Fixed bed	390–890	He, 30 cm^3/min	n.m.	–	5–73	1–3	20–92	[24]
Fixed bed	400–700	N_2 0.4l/min	120min	–	2.4–4.4	30–42.8	51.3–64	[66]
Fluidised bed	400–500	N_2	n.m.	–	n.m.	n.m.	n.m.	[21]
Fluidised bed	360–810	Air/pyr.gas N_2	1.5s	–	8–40	30–52	27–40	[69]
Continuously ablative	550	N_2	0.6s	–	n.m.	n.m.	n.m.	[49]
Continuously ablative	550	N_2	0.6s	–	n.m.	n.m.	n.m.	[70]
Flash	500–700	He	–		n.m	n.m.	n.m.	[72]
Catalytic	430	N_2, 30 ml/min	n.m.	ZSM-5	16	33.6	50.4	[74]
Catalytic	500	No gas	30 min	USY/ZSM-5	16–47	12–46	37	[23]
Catalytic	300–400	n.m.	n.m.	Al_2O_3, SiO_2, Al_2O_3: SiO_2	0.4–16.6	1.8–28.2	55.6–96	[75]
Catalytic	700	N_2, 100 ml/min	–	SiO_2, Al-MCM-41, Al-SBA-15, Beta, ZSM-5	n.m.	n.m.	n.m.	[30]
Plasma	1500	N_2, 800 ml/min	10 min	–	n.m.	n.m.	40–76.8	[76]

processes of volatile carbonization by secondary reactions are minimized, the surface properties of the carbon black are similar to the commercial ones.

In order to increase the yield of liquid products, fast or catalytic pyrolysis can be used. Alternatively, hydrogen instead of nitrogen can be used for the above purpose (hydrogenative pyrolysis). Murena et al. [47] studied an alternative route to the classic, as they used hydrogen as a medium for tyres pyrolysis. Hydrogenative pyrolysis can be done in liquid phase as it is obligatory for model compounds to be present as they function as hydrogen-donor compounds. The main advantages are: (i) lower final temperature ($350\,^{\circ}C < T < 400\,^{\circ}C$), (ii) maximization of liquid phase yield and (iii) high quality products due to absence of coking and repolymerisation reactions.

4.1. Operating parameters of pyrolysis

The operating parameters of pyrolysis are: temperature, heating rate and particle size.

4.1.1. Temperature

Gas yield increases with temperature as a result of more powerful thermal cracking in high temperatures and gas yield. Increased temperature causes raise to C_1–C_4 fraction. A remarkable increase takes place to C_{10+} fraction from (13.1 wt% to 22.9 wt%) when temperature raises from 425 °C to 600 °C, caused by Diels–Alder reactions that favour formation of aromatic compounds from olefins. Gaseous aromatic fractures C_{10+} raise with temperature while the opposite trend represents non-aromatic fractures C_5–C_{10} caused by thermal cracking and secondary reactions in higher temperatures [48].

Pyrolysis liquid's yield is almost stable on 500 °C and decreasing by raising temperatures. Higher temperatures raise lighter products' yield, as benzene and kerosene content raise with temperature. Helleur et al. [49] found similar yield (nearly 40%) and ash levels of 15.2 in tyre pyrolysis at 550 °C in an ablative reactor. De Marco et al. [50] used autoclave at different temperatures varied from 300 to 700 °C, and received char yield of 44% wt plus 12% ash.

Tar yield (C_{11+}), does not show an obvious trend in the studied temperature range and more specifically it has its maximum value at 600 °C, (11.5 wt%), with similar yields in lower temperatures of 425 °C and 500 °C (9.2 wt% and 9.3 wt%, respectively). Tar formation is originated from two opposing procedures. At first, thermal cracking of tar produces gas in high temperatures followed by the condensation of aromatic rings yields in heavy aromatic hydrocarbons [28].

Char yield obviously reduces with temperature. The removal of pyrolysis products from the hot zones, reduces the range of secondary reactions taking place that are known to raise char yield unlikely to oil yield. The specific surface of the produced char showed a significant raise by raising temperature and heating rate.

For a fluidized bed reactor Kaminsky and Sinn [51] showed an increase in aromaticity of the produced oil with temperature raise, assuming a two stage thermal process followed by secondary aromatic reactions. Wolfson et al. [52] showed that as temperatures raises from 500 °C to 900 °C, a consequent increase to aromatic compounds' volume was noticed, followed by a reduce on aliphatic fraction. Cypres and Bettens [53] referred that aliphatic compounds dominate in lower temperatures and aromatics in higher temperature. Furthermore, secondary reactions of ethylene, propene and butadiene, produce aromatic and polyaromatic compounds such as benzene, naphthalene and phenanthrene as temperature raises, with hydrogen and methane to be raised as hydrogenation occurs.

4.1.2. Heating rate

For a given temperature, the heating rate (°C/min) has a minor effect on products yield. In general, the faster the feedstock is heated to a given temperature, the less tyre-derived char and the more oil and gas are produced. Also, in a given heating rate, as temperature increases, the greater the production of benzene, pentane-2, and methanol fractions will be, and consequently the less the production of pentane-1 and ethanol fractions will be. At a given temperature, the heating value of the gas increases with the heating rate. The surface area of the solid product increases as heating rate or temperature increases [49].

Higher heating rates in small residence times along with the immediate cooling, favour liquid yield as pyrolysis gas and vapours are condensed, before reaction cracks larger M.W. molecules to gaseous products. The primary pyrolysis gases decompose into secondary tars and gases and their characteristics are time and temperature dependant. At higher temperatures the main product is gas. Tyre pyrolysis at a low heating rate produces high amounts of char and gas. A high heating rate decreases liquid yield (flash-rotary kiln-fluidized bed), while this does not happen on moderate heating rates [54].

4.1.3. Particle size

The ELTs particle size was found to influence not to a great extent pyrolysis products [55]. However, the larger the particle size is, the greater will be the amount of oils at high temperature range, while the yield of carbon black is almost constant under the same conditions [56].

4.2. Bench scale pyrolysis types and reactor configurations

The pyrolysis of end of life tyres has already been studied and reported in the International literature. Encouraging results have been obtained at different scales while using different technologies, either by the use of catalyst or not. The results concern laboratory, pilot and industrial scale reactors.

Every attempt to design and simulate pyrolysis effects on tyre sample is possible to be done and understood when operating in laboratory scale. Several researches have been conducted on laboratory scale in universities or in R&D departments. Several technologies have been developed for the pyrolysis of scrap tyres. Rotary kilns [57], ablative reactors [49], fixed bed reactors [27] and fluidised bed reactors [21].

Subsequently, several laboratory pyrolysis procedures using ELTs as feedstock are presented. It is also worth mentioning that despite the different type of reactor used, different conditions have been applied, which are also mentioned (Table 2).

4.2.1. Rotary kiln pyrolysis

Rotary kilns are used to heat solids to the point where a required chemical reaction(*s*) takes place. The rotary kiln is basically a rotating inclined cylinder. Solids retention time in the kiln is an important design factor and is set by proper selection of the diameter, length, speed, slope and internals design. There are two basic types of rotary kilns; direct fired and indirect fired.

Dıez et al. [31] compared results of tyre pyrolysis in laboratory reactor with a pilot one. He used 50 g batches of sieved tyres with a particle diameter at 0.42 mm in laboratory and about 20 kg with particle size of 1 and 5 cm in pilot reactor. The pilot reactor used was a rotary type. The temperature used for the experiments is in both cases were 550 °C.

4.2.2. Fixed bed pyrolysis

Fixed bed pyrolysis reactors are mostly used by researchers in laboratory experiments because they are easy to be constructed and operated. The majority of reactors used, were made of stainless steel or quartz and glass.

Barbooti et al. [58] pyrolysed tyre samples (25–45 g of various sizes between 2 mm and 20 mm) in a stainless steel fixed bed reactor (1.25 m in length and 0.03 m o.d.). Nitrogen (N_2) flow gas was controlled by a calibrated flow meter. Suuberg et al. [59], pyrolysed tyre samples (diameter=1 cm) in a tube surrounded by oven at 700 °C for 5 min, under nitrogen flow. Suuberg et al. [60] also used tyre samples which were pyrolysed in a tube furnace. The tyres were grounded to 35–60 mesh (250–500 μm) and were pyrolysed at a temperature up to 1000 °C for 2 h, under helium atmosphere.

Laresgoiti et al. [61] performed tyre pyrolysis experiments in a stainless steel autoclave of 3.5 dm^3 at 300 °C, 400 °C, 500 °C, 600 °C and 700 °C under nitrogen atmosphere of 1 dm^3/min, while the whole system was heated by 15 °C/min till the desired temperature, where held for 30 min. Ucar et al. [29] in their pyrolysis experiments at 550 °C, 650 °C and 800 °C used a stainless steel reactor in a semi-batch process under nitrogen flow at 25 ml/min for 10 min. About 130 g of tyre samples were loaded to the reactor which was heated at a rate of 7 °C/min till the final pyrolysis temperature, where held for 1 h. Jitkarnka et al. [62] placed used tyre samples 1 g, (0.5–1.4 mm diameter) in a U-tube reactor under nitrogen flow (30 ml/min) for 30 min. Cao et al. [63] have co-polymerised tyres and sawdust in a complex pyrolysis apparatus that included apart from the tubular reactor a desulphurizing one. Arabiourrutia et al. [25] made their experiments in a conical bed with nozzle, under nitrogen flow with a gas residence time from 20 ms up to a few seconds, at 425 °C, 500 °C, 550 °C and 610 °C. Paradela et al. [64] used a stainless steel Hastelloy C276 alloy autoclave. They used a mixture of 3 residual wastes and more specifically tyres up to 10%. Aranda et al. [65] produced pyrolytic carbon black in an experimental assembly which included a preheater for the carrier gas, a 2.4 cm internal diameter stainless steel fixed bed reactor followed by a condenser, a filter and finally a burner were pyrolysis gas products were burned. The used tyre sample was 60 g, with a particle diameter <1 mm. Berrueco et al. [66] performed ELTs pyrolysis in a system consisting of an externally heated fixed bed. The stainless steel reactor is 5.5 cm in diameter and 40 cm in height. Four K-type thermocouples were located at different heights inside the reactor and bed. The reactor was loaded with 300 g of sample. A nitrogen flowrate of 0.4 l/min was used in the tests as purge gas. The pyrolysis products (gas and liquids) evolving from the reactor passed through a heat exchange system. The heaviest liquid fractions were collected by a counter current water-cooled heat exchanger.

Dıez et al. [67] used a quartz tube of 40 cm long and 7 cm in diameter in a heating rate of 5–60 °C/min under nitrogen flow of 200 ml/min. The laboratory reactor consisted of a quartz tube 40 cm long and 7 cm in diameter, the heating rate varied from 5 °C/min to 60 °C/min, under a steady nitrogen flow of 200 ml/min and at a temperature range 500–600 °C. Williams et al. [21] used a bench-scale fixed-bed pyrolyser for tyre size of l–3 cm^2. He also used a stainless steel reactor with dimensions of 10 cm diameter ⁎15 cm high. The total weight of ELT used was 150 g. The heating rate reaches up to 5 °C/min till the final temperature of 570 °C where held for 1 h. Nitrogen flow was stable and the residence time was 30 s [68]. Thermal decomposition produces free radicals of high activity [54].

Zabaniotou et al. [24] used a plexiglass captive sample reactor. End of life tyres were shredded in pieces less than 500 mm. About 200 mg were spread to a stainless steel plate, which was inserted between electrodes. The whole device was under helium flow (30 cm^3/min) in a temperature range 390–890 °C, with a heating rate of 70–90 °C/s. The plexiglass tubular reactor had internal diameter of 7 cm and 12 cm high and was accomplised with 2 pairs of stainless steel SS316 flanges.

4.2.3. Fluidized bed pyrolysis

Fluidised bed reactors are more difficult to operate and thus the studies where a fluidised pyrolyser was used are few. However, fluidised bed reactors have the following advantages: long residence time which contributes to secondary reactions and lower temperature and heating rate that favor carbonization which reduces oil yield. Pyrolysis in a fluidised bed is characterised as fast pyrolysis directly producing a liquid fuel, which is beneficial when tyre resources are remote from where the energy is required, since the liquid can be readily stored and transported.

Williams et al. [21] used a stainless steel bench-scale fluidized reactor with dimensions of 10 cm diameter × 70 cm high, with a 20 cm diameter × 17 cm in the upper body in order to reduce gas velocity. The waste material was fed by gravity via a rotary valve feeder at an accurately metered rate of between 0.75 kg/h and 1.2 kg/h. The fluidizing gas was nitrogen, preheated to 400 °C. The reactor temperature was maintained at 400 °C, 450 °C, 500 °C or 550 °C by the use of separate external heaters for the fluidized bed, freeboard and cyclone. The bed material was silica sand of mean size 250 μm, with a static bed depth of 8 cm. Fluidization was maintained at the minimum fluidizing velocity of 0.027 m/s at 550 °C.

Dai et al. [69] used a CFB with quartz sand as the circulating fluidizing agent. The fluidized gas is nitrogen heated at 400 °C. The reactor's temperature was held at 500. The main trends observed were: (a) long residence time which contributes to secondary reactions and (b) the lower temperature and heating rate that favor carbonization, which reduces oil yield. Thus, the most important components in pyrolytic oil are aromatics, followed by alkanes, non-hydro-carbons and asphalt.

4.2.4. Ablative reactor pyrolysis

Ablative pyrolysis is less used. Ablation characterizes the phenomena occurring when a solid, submitted to a high external heat flux density, gives rise to solids, liquids and/or gases that can be rapidly and continuously eliminated. Ablation can be exploited for carrying out the fast pyrolysis of materials such as tyres. Tyres are pressed against a hot surface (contact ablative pyrolysis) or intercept a concentrated radiation (radiant ablative pyrolysis).

Helleur et al. [49] performed car tyre pyrolysis in an ablative reactor and concluded that ash content % in char is high and between 9% to 12% and sulphur content of about 2%. Stanciulescu et al. [70] used an ablative pyrolysis reactor at 550 °C, with residence time of 0.6 s, under nitrogen flow and with a tyre size of 1 cm.

4.2.5. Flash pyrolysis

Flash-pyrolysis is characterized by high heating rates, temperatures between 450 °C and 600 °C, and short residence times of less than one second. These conditions prevent cracking of the vapors into non-condensable gases, maximizing the liquid product yield [71]. Aguado et al. [72] studied tyre flash pyrolysis in a fast heating microreactor (heating rate up to 20,000 K/s assuring a better contact between gas–solid) with an extremely small residence time (below 100 ms) that minimizes every secondary reactions. ELTs samples that used were of about 0.2 mm and at temperatures of 500 °C, 600 °C and 700 °C. Fabbri et al. [73] used a quartz tube to be a probe for a CDS 1000 pyroprobe that is accomplished with a temperature-resistant platinum fibre while

the exit is connected to a monitoring unit used to determine XAD-2 resin on produced gas.

4.2.6. Catalytic pyrolysis

Researchers used various catalysts in tyres pyrolysis. The most used catalysts are Y-type zeolite, ZSM-5 and Al_2O_3. The influence of the catalyst is to reduce the yield of oil with a consequent increase in the gas yield. Single ring aromatic hydrocarbons, benzene, toluene and xylenes present in the oils, can markedly increase in the presence of the catalyst. Naphthalene and alkylated naphthalenes show a similar marked increase in the concentration when a catalyst was present. The Y-type zeolite catalyst of larger pore size and higher surface activity was found to produce higher concentrations of aromatic compounds compared to the ZSM-5 catalyst.

Qu et al. [74] pyrolysed used tyre samples in a stainless steel reactor (60 ml volume) in batch operation and used catalysts. They mixed approximately 10 g of end of life tyres with 0.005 g of ZSM-5. The nitrogen flow was set at 30 ml/min. The reactor was initially heated up to 120 °C for 20 min. Then, it was held at this temperature for 60 min and then by a heating rate 10 °C/min, was heated to 430 °C until no liquid product was produced.

Boxiong et al. [23] using catalytic pyrolysis reactor, reached the result that zeolite USY catalyst and ZSM-5 catalyst reduced oil yield, maximizing simultaneously gas yield. Shah et al. [75] studied catalytic pyrolysis of End of Life Tyres and concluded that the use of Al_2O_3 as a catalyst produced higher liquid yield and reduced gas yield. San Miguel et al. [30] produced larger fraction of light hydrocarbons and with ash content on solid products to the levels of 3.7%. Olazar et al. [26] used a catalytic fixed bed reactor of 82 mm height and 5 mm internal diameter that contains the catalyst.

4.2.7. Plasma pyrolysis

Thermal plasma pyrolysis refers to solid reaction with limited oxygen and high temperatures to produce gaseous and solid products. When tyre particles are inserted to plasma, the volatile matter is released and cracked, raising hydrogen and light hydrocarbons content such as methane and acetylene.

There are 4 detected stages of plasma pyrolysis that include extremely fast particle heating originated from plasma jet, an enormous release of volatile matter from tyre particles, ultra fast gasification of homogenous phase and rapid heating and mass exchange. Thermal plasma pyrolysis has several advantages such as high heating transfer rate, desired properties of pyrolysis products, high capability of removing/destroying harmful substances. Thermal plasma reactors demand high amounts of energy for high temperatures. Plasma pyrolysis yields only 2 streams of products: pyrolytic gas that could be used as fuel and pyrolytic char. This is due to the fact that during plasma discharge there is a large amount of highly active species that include ions, free radicals, activated atoms and molecules. Heavy hydrocarbon compounds are released from the volatile content of tyres and can be rapidly cracked (decomposing), giving raise to hydrogen and lighter hydrocarbon content [76].

Huang et al. [76] used batch samples with different tyre particle size (200–600 μm) in a plasma pyrolysis apparatus. The high frequency plasma generator (power output: 0–2000 W) was made of quartz with internal diameter = 16 mm, external diameter = 18 mm and length at 500 mm and 2 cylindrical copper electrodes. This operation was held under high energy, high temperatures (1200–1800 K) and low pressure. Tang et al. [77] used a plasma pyrolysis reactor with a maximum electric power input of 55 kV A. It consisted of two main parts: the plasma generator and the reaction chamber.

4.2.8. Molten salt pyrolysis

Molten-salt destruction is an alternative pyrolysis route. Its main characteristic is that, as a heat transfer and reaction/scrubbing medium to destroy hazardous materials, a molten, turbulent bed of salt is used, such as sodium carbonate. Shredded solid waste is injected with air under the surface of the molten salt. Hot gases (carbon dioxide, steam, and unreacted air) rise through the molten salt bath, pass through a secondary reaction zone and through an off gas cleanup system before discharging to the atmosphere. The rest of pyrolysis by-products, react with the alkaline molten salt forming inorganic products that are retained in the melt. Spent molten salt containing ash, is drawn away from the reactor, cooled and placed in landfills [78].

4.2.9. Microwave pyrolysis

The microwave process applies thermal energy very quickly and uniformly on the waste rubber. Apart from the short reaction time, microwave pyrolysis is characterised by high heating efficiency and as a result polymers such as ELTs can be easily heated despite their low thermal conductivity. However, any vulcanized rubber used in the microwave process must be sufficiently polar in structure so that the microwave energy can be absorbed at the appropriate rate to make devulcanization viable [79].

4.3. Pilot scale pyrolysis

As described above, there were plenty, laboratory and bench scale, studies on tyres pyrolysis, carried out. Pilot scale pyrolysis studies are fewer in the literature. Dıez et al. [31] used pilot pyrolysis of 20 kg feeding tyres of particle size of 1 cm and 5 cm. The pilot reactor used was a rotary kiln. The temperature used for the experiments was 550 °C. López et al. [80] used a pilot conical fixed bed reactor with a nozzle. Its conical geometry sets the reactor as the best practice for high temperature procedures since it assures intense contact between gas–solid. Furthermore, this type of reactor prevents liquid loss from the bed with aggregation of particles even under severe conditions, involving very sticky particles being the same time suitable for continuous operation, important fact for tyre pyrolysis.

EU in order to cope with the conservation of resources and waste valorisation has funded two projects for pilot/demonstration scale on tyres pyrolysis. TYGRE project [81] focuses the attention to the problem of the waste tyres, by promoting their treatment through the development of a thermal process mainly devoted to the production of ceramic materials. TYGRE is under funding of the current 7FP promoted projects aimed at developing technologies for recovering high added-value products from selected waste streams and funding pilot schemes.

Another project concerning a pilot scale plant funded by EU LIFE Plus program, the DEPOTEC project [82], poses a depolymerisation process that will add value to the end of life tyres, by producing products that can be used as substitute carbon filler materials, in the rubber manufacturing process, and activated carbon as a filter in water cleaning, with parallel reduction in stockpiling of tyres. The project aims to demonstrate the viability of future mainstreaming of the process, by processing a significant volume of End-of-Life Tyres into a microporous carbon material with adsorbent properties over the duration of the project. The most effective testing procedures for gauging the technical quality of the products of this process will be assessed and the project will also contribute to the development of a comprehensive series of environmental standards that will facilitate the accreditation of the products of recycling of ELTs (e.g., through the European Eco-Label). The end result will be the

development of a technology that can be used throughout Europe to enable the production of high added value products from waste.

4.4. Industrial scale pyrolysis

The previous decade was characterized by efforts made to scale up all the previous knowledge about tyre pyrolysis, taking under consideration every aspect of the process, minimizing at the same time every possible drawback. The main idea was to create industrial plants producing mainly liquids, using as raw material ELTs or other similar polymeric products in a self-sustained way obeying simultaneously to every strict environmental legislation.

Many attempts have progressed, creating a wide range of industrial appliances aiming at fuel and material recovery. The manufacturers located around the globe give certain solutions to energy valorisation of ELTs. More specifically, *Metso company* uses a large scale rotary pyrolysis unit. The ELTs decompose with the produced carbon char heading to final processing, and gas to an oil condensing system. The non-condensable gases (NCG's) can be used as fuel for power generation or other direct fired uses. There is an independent oil condensing system developed for the recovery of oil. Carbon black produced from the pilot plant can be successfully used on tyre manufacturing and industrial rubber products [83]. Table 3 presents the current technological tendencies along with important data about the pyrolysis plants.

Klean industries use several types of pyrolysis liquefaction systems; among them are rotary kiln and the fluidized bed. Some systems provide direct heat, others indirect, and both continuous feed and batch feed variations are available. There are a number of different types of liquefaction processes, all of which differ significantly with respect to residence time (for the waste material), heating rate, temperature and by-products. These range from carbonization taking up to 24 h and producing coal at low temperatures, to flash pyrolysis which takes less than a second and produces syngas at extremely high temperatures [84].

Table 3
Products from industrial scale pyrolysis.

Reactor type	Capacity	Feedstock particle size	Products	Company
Indirectly fired kiln, grinding circuit, oil condensing and gas cleaning system. $T=450$ °C	100 kg/h	−50 mm tyre shreds	Steel:11% Pyro Black:31% Oil Product:25% Gas: 33%	Metso–Minerals Pyro Systems, USA [83]
Pyrolysis liquefaction includes rotary kiln, rotary hearth unit, and the fluidized bed $T=430$ °C	100 t/day	Whole tyre	3 MWe electricity 5,000 TPA CBp 10,000 TPA diesel grade fuel oil 3,600 TPA steel 75,000 TPA Carbon Dioxide emission offset	Klean Industries, TPP, Kouei international [84]
Depolymerisation with catalysts (normal temperature and pressure)	Up to 20000 t/yr	Tyre chips $>50\times50$ mm	Fuel oil: 45–50% Carbon black: 35–38% Steel wire: 9–11% Flammable gas: 5–7%	Jiangyin Xinda Machinery Co.,Ltd [85]
Batch pyrolysis reactor $T>400$ °C		Whole tyre	Oil: 35–45% Char and carbon black: 30–40% Gas: 12–15% Steel: 10–12%	JINGCHENG INDIA [86]
Rotary pyrolysis reactor 350 °C $<T<$ 450 °C	Up to 10 t/day	$>0.72\times1.2$ m	Fuel oil: 45–50% Carbon black: 25–30% Steel wire: 10–15% Gas: 5%	Xinxiang Huayin Co.LTD [87]
Batch pyrolysis reactor 350 °C $<T<$ 450 °C	Various	Whole tyre	Fuel oil: 40–45% Carbon black: 28–33 Steel wire: 8–12% Flammable gas: 8–10%	Pyrocrat [88]
Indirect Rotary Kiln	Various	Whole tyre	Crude oil: 30% Carbon black: 30% Steel wire: 10% Gas: 30%	Pyreco [89]
Modular pyrolysis Steam Cycle (MPSC) system in a rotary kiln using an indirect, external source of heat, 400 °C $<T<$ 600 °C	Up to 20 t/day		Crude oil: 27% Gas: 45%	Splainex [90]
Batch Horizontal reactor $T=400$ °C	15 t/day		Diesel 30% Gasoline 5% Steel 10% Carbon black 40% Natural gas 5%	Hanocorp–Pyrogen [91]

Pyrocrat technology is an industrial solution of catalytic pyrolysis. Its main characteristics are lower reaction temperature (350 °C to 475 °C), zero emissions, lesser reaction time and more energy savings [88].

Splainex technology uses a Modular Pyrolysis Steam Cycle (MPSC) system waste is thermally degraded in a rotary kiln using an indirect, external source of heat, at temperatures of 400–600 °C in the absence of oxygen. The volatile portion of the feedstock is thermally decomposed, producing syngas which is sent into a boiler, producing steam for power generation, with the flue gas treated in an emission control sub-system. Char from pyrolysis kiln is further treated to generate extra syngas to be used in the process [90].

Hanocorp/Pyrogen uses the "Reverse Green Technology", a feedback system which sends back pollution and energy; after a certain working period the system works without external supplies of energy. The reversed processing of smoke cleaning system is characterized by quick absorption and desorption, which can eliminate all the infectants such as: H_2S, CO, CO_2, SO_2, SO_3, NO, NO_2, CS_2, NH_3, as well as other oil organic compound and solid particles [91].

4.5. Pyrolysis products

ELTs pyrolysis produces three principal products: gas, oil, and char. The gas and oil, which comprise about a half of the pyrolysis product by weight, have energy content similar to conventional fuels. The gas, known as syngas (with low heat properties) can be used in various appliances reducing the energy needs of the tyre pyrolysis plant. The oil is characterised by decent energy content compared to diesel oil.

Pyrolysis char produced in this process has low commercial value, as it consists of a mixture of the different types of carbon blacks used in tyre manufacturing. Therefore, the resulting product does not have the same quality as those of the original carbon blacks used in the manufacturing of tyres.

Carbon black Char is a fine particulate composed of carbon black, ash, and other inorganic materials, such as zinc oxide, carbonates, and silicates. In order to improve its characteristics, for the purpose of using it to develop new products, particle size reduction may be carried out to upgrade the pyrolysis char.

Another possibility is to use pyrolysis char as activated carbon. Nowadays, upgrading techniques are considered to be economically viable in view of the market demand for the product.

Different classification of pyrolysis products was made by López et al. [80]. According to him pyrolysis products are categorised in 5 teams depending on their hydrocarbon number: Gaseous (C_1–C_4 hydrocarbons), liquids (non-aromatic C_5–C_{10} hydrocarbons), aromatic liquids (single ring $C_{10}-$ aromatic hydrocarbons), tar (C_{11+} aromatic or not) and char.

4.5.1. Gas product composition

The gaseous products from tyre pyrolysis include hydrogen, carbon dioxide, carbon monoxide, methane, ethane and butadiene. Lower concentrations of propane, propene, butane and other hydrocarbon gases were also detected. Increased temperature and heating rate, results to evolution on gases. The volume of each gas increases with increased heating rate.

Gases produced have high LHV values between 34.6 MJ/mm^3 and 40.0 MJ/mm^3. As temperature rises, the heavier hydrocarbons are cracked, giving rise to lighter ones, methane and hydrogen [53]. Consequently, the gas samples become enriched with the lighter hydrocarbons as the temperature increases [92]. Gas yield raises as oil yield decreases. Gas production is favoured by long residence times and high temperatures.

Zabaniotou et al. [24] reached a result that an increase at gas yield can be accomplished by a decrease of the pyrolitic liquids due to stronger thermal scission that happens in higher temperatures. Hydrogen shows maximum production at 550 °C, suggesting that hydrogen generation increases with temperature. Pyrolysis under these experimental conditions indicate that the cracking reactions prevail (increasing the yield to hydrocarbons, CH_4, C_2, C_3 and C_4), whilst the aromatization and cyclization reactions, which increase H_2 and aromatic production, would have a minor influence [65].

The CO_x components must be derived from the cracking of organic compounds, such as stearic acid, extender oils, etc., contained in tyres, and even from inorganic components of tyres, such as $CaCO_3$, metal oxides, etc. Significant amounts of CO_x in tyre-pyrolysis gases were also detected. Furthermore, the higher the final temperature of pyrolysis is, the less CO_2 is produced, while CO increases probably as a consequence of the secondary reactions taking place during the pyrolysis process. During secondary reactions, CO is formed by reactions in gas phase between CO_2 and hydrocarbons or from other cracking reactions (homogeneous phase reactions) [63,65,93]. González et al. reached to similar results but he also considered that the CO_x presence is due to decarbonilation, decarboxilation reactions and char secondary reactions [94].

Light hydrocarbons are generated from the rupture of SBR which also forms short aliphatic chains. Light hydrocarbons are also formed from secondary cracking reactions which are favoured by the high temperatures. The main fraction obtained in all cases is, the fraction containing C_4 hydrocarbons. The main substance in this fraction is isobutylene, with a percentage of 85 wt%. Berrueco et al. [66], concluded that the heavier hydrocarbons are predominantly generated at lower temperatures, and are derived from the direct breakdown or depolymerisation of the styrene–butadiene polymer.

The oxygen and nitrogen in some samples, is explained by the samples being contaminated by air, as they are in the same proportion as in the atmosphere [63]. The gas fraction shows fairly low values for sulphur, probably in the form of hydrogen sulphide (H_2S). Another form is sulphidric acid that comes from the sulphur links of the vulcanised rubber structure; nevertheless, its concentration is rather low, even though the tyre sample contains 1.5 wt% sulphur [49].

The gases generated in the process of pyrolysis of tyres have high GCV. As temperature raises, GCV values drop. Literature review shows that CO_x increases with temperature and that the proportion of longer hydrocarbons, which have the greatest calorific values, is lower at the higher temperatures [93]. Further data are presented on Table 4.

Additionally, characteristics from biogas and gasification gas are also presented in the same table, since they are typical representatives of combustible gases that can be used in various appliances. Biogas primarily consists of methane and carbon dioxide (about 60% methane and 40% carbon dioxide) and has lower calorific value than natural gas. Methane in biogas mixes readily with air and has high octane rating, making it a suitable fuel for spark ignition engines. The energy utilization of biogas is maximized when it is converted into electricity. Moreover, either biomass or biomass residues can be gasified under higher temperatures than the usual of pyrolysis, producing syngas, which can be used directly to I.C.E. for electricity production.

4.5.2. Liquid product composition

There is a large variety of chemicals/constituents into pyrolysis oil. More specifically aromatics, non-aromatics, oxygenated aromatics, oxygenated non-aromatics, nitrogenated aromatics or

Table 4
Composition of gaseous products (wt%).

Type	PCT	TT	PCT	PCT	PCT	PCT	Tyre shred	Tyre shred	Tyre shred	Tyre shred (LR)	Tyre shred (PP1)	PCT	PCT	PCT	PCT
Temperature	**650**	**650**	**400**	**500**	**550**	**700**	**350**	**450**	**550**	**550**	**550**	**400**	**500**	**600**	700
C_1	23.9	24.2	1	4.3	5.6	5.42	20	24	26	22	26.7	4.4	19.8	20	20.6
C_2	13.3	12.5	0.7	2.2	2.6	2.7	29	26	20	27	21.6	8.8	18.5	18.7	17
C_3	11.8	12.5	0.5	1.3	1.5	1.5	12	9	6	10.3	4.6	8.5	10.8	10.6	7.7
C_4	7.6	9.5	3.4	2.4	1.9	2.4	5.7	4.3	2.8	4.9	4.1	36.9	21.3	21.9	19.8
C_5	10.7	12.2	0.02	0.02	0.02	0.03	3	2	1.1	2.5	1.6	16.5	7.6	7.4	6.7
C_6	0.2	0.2	0.3	0.36	0.3	0.48	1	0.2	0.1	0.6	0.1	7.3	2.8	2.5	2.5
CO	1.1	2	1.1	0.25	0.26	0.38	1	1.1	1.6	1.1	2.5	4.2	4.8	6.5	10.4
CO_2	2.4	6.1	1.4	1	0.78	1.2	2.3	1.9	1.4	2	6.6	10.7	9.4	8.8	11.4
O_2	2.7	1.5	–	–	–	–	–	–	–	–	–	–	–	–	–
H_2	26	19	2.6	14.2	17.8	10	24	30	40	27.8	29.5	–	–	–	–
Heating value (MJ/kg)															
HHV	60–65	60–65	–	–	–	–	55.01	47.66	39.6	49.1	41.8	84	75.5	75.3	68.5
LHV	–	–	5.5	7.8	8.3	9	50.8	43.83	36.16	45.2	38.5	–	–	–	–
Reference	[29]	[29]	[69]	[69]	[69]	[69]	[64]	[64]	[64]	[31]	[31]	[50]	[50]	[50]	[50]

Type	Tyre shred	Tyre shred	Tyre shred	SBR	Tyre shred	PCT	Tyre shred	Tyre shred	Biogas*	Olive Kernel (gasification) **
Temperature	**550**	**900**	**550**	**> 700**	**740**	**700**	**780**	**750**	–	**750**
C_1	9.9	24.1	21.32	18.41	48.8	32.1	34.35	35.43	65	3.75
C_2	5.9	10.3	6.5	23.84	12.44	8.94	30.61	14.03	–	1.81
C_3	5.3	6.2	5.43	42.56	3.35	7.89	11.9	8.77	–	n.m.
C_4	38.1	24.8	35.39	–	1.43	2.4	4.76	0.7	–	n.m.
C_5	–	–	**< 2**	–	**22.48**	**30.52**	**15.64**	**16.14**	–	n.m.
C_6	–	–		–					–	n.m.
CO	**9**	**13**	**4.51**	0.51	–	7.89	–	13.3	–	14.26
CO_2				3.26	–	8.94	–	7.01	32	19.42
O_2	–	–		–		–		–	–	–
H_2	7.9	8.4	22.27	0.8	3.82	2.1	2.32	4.56	–	23.98
Heating value (MJ/kg)										
HHV	65.6	57.5	46.5	–	–	–	–	–	25	6.54
LHV	–	–	–	–	–	–	–	–	–	–
Reference	[35]	[35]	[36]	[40]	[41]	[41]	[41]	[41]	[94]	[95]

* Biogas was produced from biomethanation of jatropha and pongamia oil seed cakes. Other gases are limited to about 3%.
** Equivalence ratio for olive kernel gasification ER=0.2.

nitrosulphurated aromatics consist the complex mixture of pyrolytic oil. The aromatic characteristics are mainly due to aromatic nature of polymeric material, to the existence of styrene–butadiene rubber, and on the other hand to the cyclisation of olefins structures followed by dehydration reactions [28].

There is a great variety of compounds with more than 1% percentage such as toluene, dimethylcyclohexenes, ethylbenzene, xylenes, styrene, methyloctene, and limonene in liquid from pyrolysis. There are also plenty of oxygenated compound such as phenols, acids, etc., and their concentration is up to 2–3%. Those compounds are due to thermal decomposition of oxygenated compounds of tyre, such as stearic acid, extender oils [23].

There are also compounds with nitrogen, detected on pyrolysis oils ($\approx$ 3%). Those compounds may be originated from vulcanization agents used in tyre manufacturing and contain sulphur or nitrogen such as benzothiazoles, thioureas, amines, etc. Benzothiazol concentration on pyrolysis oil is relatively high ($\approx$ 1%) since benzothiazol is a vulcanization agent widely used on tyre manufacturing [61].

Benzene, toluene and xylenes are very important chemicals. They are used as primary feedstocks to produce plastics, resins, fibres, surfactants, dyestuffs and pharmaceuticals, and long-chained alkylbenzenes that can be used as surfactants. Xylenes are important industrial chemicals. *O*-Xylene is used as a phthalic anhydride to produce plasticizers and dyes, *m*-xylene derivatives are used on polyesteric resins and fibre industries and *p*-xylene derivatives on polyesteric fibres. Toluene has a wide range of appliances and is mostly used on pesticides, dyestuffs, surfactants and solvents production.

Elemental analysis is used to characterize tyre pyrolysis oil and the results are similar to those of commercial oils. The forms of hydrocarbons are identified by HNMR analysis. A FT-IR absorbance frequency spectrum is used to identify functional groups on tyre pyrolysis oil. More specifically, compounds that can be identified are alkanes 1–4, alkenes and aromatic compounds as benzene, toluene, xylene, styrene and 2–6 ring PAH along with alkyl-derivatives [56].

Ucar et al. [29] characterised by terms of fuel and chemical composition the tyre pyrolysis derived oil. The pyrolytic liquids from PCT and TT are called PCTO and TTO, respectively. Specific gravity of pyrolytic oil was found to be higher than of commercial ones. Pyrolytic oil viscosity from TT and PCT is in the range of commercial diesel. The flashpoint of them is lower than of diesel oils. Similarly heating values are also similar to commercial ones, proof that they can be easily used for the pyrolysis plant energy needs.

The boiling point of the pyrolysis products is wide and has no significant difference despite temperature changes. At 550 °C, PCTO contains almost 50% gasoline (boiling point < 172 °C), whereas TTO contains only 40%. The initial boiling point was lower than of diesel oil but higher of common benzene. Consequently, pyrolytic oil from PCT and TT can be mixed with gasoline or diesel after hydrogenation or desulphurization [29].

PCTO mainly contains ethyl benzene, toluene, styrene that could produce propyl benzene, isopropyl benzene, a-methyl styrene, polycyclic aromatic hydrocarbons (PAH). As for PCTO and TTO, some aromatic hydrocarbons contain sulphur, nitrogen and oxygen, and smaller compounds with a relatively small

Table 5
Characteristics of pyrolytic oil.

Oil type	PCTO(650 °C)	TTO (650 °C)	PCTO (450–650 °C)	PCTO (300–700 °C)	PCTO	PCTO	PCTO	PCTO	PCTO
Ultimate analysis (wt%)									
C	85.57	86.47	–	~86	86.87	68.91	79.61	81.18	–
H	10.35	11.73	–	~10	10.07	9.6	10.04	10.92	–
N	< 1	< 1	–	< 0.5	1.18	2.05	0.94	1.85	–
S	1.35	0.83	0.95	~1.2	0.9	1.07	0.11	0.031	0.9
Specific gravity (g/cm^3)	0.943	0.913	0.935	–	0.845	0.82	0.83	0.935	0.945
Viscosity at 40 °C (cst)	4.6224	3.853	3.2	–	3.4	0.95	1.01	3.2	3.8
Flashpoint (°C)	< 30	< 30	43	–	60	61	65	43	n.m.
GCV (MJ/kg^1)	41.6	42.7	n.m.	42.6	43.34	42.61	42.66	38	43.34
Reference	[29]	[29]	[113]	[61]	[99]	[100]	[100]	[101]	[102]

Oil type	Raw TDF	PCTO	PCTO	TTO	PCTO (700 °C)	PCTO	Diesel	Gasoline	Biodiesel	Vegetable oil (Mahua)	Rapeseed bio-oil
Ultimate analysis (wt%)											
C	–	84.09	85.4	87.57	91	83.48	87.4	85.4	77	–	73.74
H	–	9.75	11.4	10.35	8.17	13.12	12.1	14.1	12	–	10.69
N	–	0.39	0.4	< 1	1.39	0.22	370ppm	200ppm	–	–	4.65
S	1.13	1.37	0.6	1.35	1.05	0.72	1.39	280ppm	0.015	–	0.11
Specific gravity (g/cm^3)	0.944	0.994	0.9	0.943	–	0.9239	0.838	0.78	0.88	0.904	0.993
Viscosity at 40 °C (cst)	5.06	6.61	2.81	4.62	–	3.77	2.1	–	1.9–6.0	37.18	62
Flashpoint(°C)	42.5	–	20	< 30	–	43	54	−43	> 130	238	62
GCV (MJ/kg^1)	39.9	42.6	43.27	–	–	38	45.5	43.9	–	38.66	36.4
Reference	[103]	[34]	[36]	[104]	[105]	[106]	[100]	[100]	[107]	[108]	[109]

Table 6
Chemical analysis of pyrolytic oil [28,57].

Type of oil	Temperature (°C)	Aromatics	Paraffins	Olefins	Reference
PCTO	550	41.54	54.55	3.91	[29]
	650	41.21	54.85	3.94	
	800	41.15	54.88	3.97	
TTO	550	15.41	64.12	20.47	
	650	15.29	64.31	20.4	
	800	15.22	64.45	20.33	
PCTO	300	53.4			[61]
	400	66.6			
	500	70.9			
	600	74			
	700	74.8			
PCTO	n.m.	36.14	42.68	21.18	[34]
PCTO	< 440	< 5	29.96	65.04	[110]

Table 7
Simulate distillation and elemental analysis results of pyrolytic oil.

Fraction	%wt	Analytical method
Gasoline	94.1	ASTM D 2887_08
Diesel	5.1	ASTM D 2887_08
Residue	0.8	ASTM D 2887_08
Carbon	83.53	ASTM D 5291
Hydrogen	13.35	ASTM D 5291

amount of constituents. According to the HNMR results, aromatic content of PCTO was found higher than of TTO [29].

The aromatic content of pyrolytic oil is due to the aromatic structure of tyre but also from the cyclization of olefinic structure followed by dehydrogenation and Diels–Alder reactions. It is also believed that the creation of aromatic hydrocarbons comes from alkenes through Diels–Alder reactions that take place during PCT pyrolysis, since they mainly contain Butadiene Rubber (BR). The increased aromaticity of pyrolytic oils refers to reactions among compounds with lower M.W. that produce compounds with increased molecular weights. The differences in the aromatic content of oils can be attributed to the dissimilarities of the raw material (NR content: PCT 35 wt%; TT 51 wt%, respectively), or that limonene and/or limonene precursors may have reacted to the pyrolytic products from BR components. There is a raise on number and mean M.W. with temperature raise. A smaller portion of oil contains compounds with high M.W. This is explained by the raise of aromatics followed by the reduce of aliphatics. Pyrolysis oil mass reaches a maximum between 420 °C and 600 °C and much smaller amount of oil is produced till 720 °C [29].

Sulphur content is small but not negligible, since there are strict regulations for fuels containing sulphur [97]. Sulphur on PCTO and TTO is higher than of commercial ones. Pyrolytic oils from PCT generally contain higher sulphur content than TT. Williams et al. [21] concluded that a great number of PASH is present in pyrolytic liquids and the PASH content in them raises with temperature. This is due to aromatic reactions Diels–Alder. Williams et al. [98] also showed that when catalyst is present, the oil yield reduces and consequently gas yield rises. The derived oil from catalytic pyrolysis has a large amount of single aromatic compounds, and toluene reached a maximum content on oil of 24 wt%, benzene 5 wt%, *m*/*p*-xylenes 20 wt% and *o*-xylene 7 wt%. Aromatic hydrocarbons' yield in the produced oil relates to pore size, that affects selectivity, plus silica/alumina ratio affecting the number of catalytically active sites on catalytic surface.

As a conclusion, there is an increase on PAH compounds (naphthalenes, phenanthrenes, fluorenes, diphenyls), with temperature due to aromatic compounds and olefins followed by cyclisation of olefinic chains and dehydration.

The pyrolytic oil from our laboratory pyrolyser along with an industrial scale batch pyrolysis unit were analysed and the pyrolytic oil has been further processed in a two stage desulphurization and hydrogenation upgrading process. Its water percentage and calorific value were determined (0.4314% wt, 42.6 MJ/kg, respectively).

Characteristics of oil are presented in Tables 5–7. Table 5 also contains useful data on biodiesel, rapeseed pyrolysis oil and also vegetable oil. The most important characteristics of common transport fuels (diesel and gasoline) are also presented.

4.5.3. Solid product (char and carbon black) characteristics

A solid product termed tyre-derived char or tyre-derived carbon char is produced by tyre pyrolysis. The solid product can be further processed to acquire specific characteristics, so as to meet specifications for carbon black, or it can be marketed directly. The chars obtained in tyre pyrolysis are mainly mesoporous materials with a low surface area but suitable as adsorbents after activation processes. However, due to the high calorific value of these solid residues, they can also be combusted for energy recovering [111].

Carbon black quality is defined by a number of different properties including particle size and specific surface. Kawakami et al. [112] showed that natural properties of the produced char from carbon black tyres, such as elongation, hardness depend on tyre type and pyrolysis conditions. Carbon black that comes from tyre pyrolysis has similar or even better properties to commercially available carbon black. This is due to high ash content and the presence of solid hydrocarbons. The received char can be used if activated with steam at 750–950 °C, or non-activated in more simple appliances such as belts. Specific surface of received char seems to increase by pyrolysis temperature [113]. The solid yield from tyre pyrolysis contains carbon black and solid hydrocarbon residue that can be reduced when raising pyrolysis temperature and heating rate. When removing solid hydrocarbon residue, char's specific surface can be augmented improving simultaneously carbon black's properties. Its specific surface is comparable to carbon black used for tyre manufacturing (N-351 and N-650 show specific surfaces at 73 m^2/g and 38 m^2/g, respectively).

Tyre plasma pyrolysis char contains more than 80 wt% of elemental carbon and there is specific surface comparable to commercial carbon black. However, the sample contains high levels of ash mostly of its additives, e.g., ZnO, and other inorganics required on tyre manufacturing. Several anthraceous structures that come from plasma pyrolysis can produce high specific surface catalysts and electronic appliances such as ac supercapacitors etc [76].

Pyrolytic char in order to be reused, it is preferred to be under 1% of sulphur content. In general, approximately half of the original sulphur remained in the solid char rather than being released as condensed vapor phase within the range of 350–850 °C [114]. Steam activation can remove sulphur from the derived char [115]. The residual sulphur in solid products may reach levels of 80–98% of the initial amount, showing that sulphur during plasma pyrolysis deposits mainly on solids. In char, sulphur is chemically bonded with the form of non-volatile inorganic sulphides and elemental sulphur along with traces of organic sulphides [87].

Data on char and carbon material characteristics are presented in Table 8. Moreover, characteristics from char of pitch pine pyrolysis are also presented and compared to chars from tires. The elemental analyses show similar results, however S_{BET} values

Table 8
Characteristics of char obtained by end of life tyres pyrolysis.

Pyrolysis reactor type	Continuous flash	Continuous ablative	Bench scale monohearth	SETARAM TG DTA-92	Rotary kiln	Fixed bed	Horizontal oven
Ultimate analysis (wt%)							
C	86.92	80.6	71	90.27	94.9	95.9	–
H	1.17	1.3	–	0.26	0.7	0.5	–
N	3.34	0.3	–	0.16	0.3	0.2	–
S	0.51	2	2.8	1.22	3.8	3.3	–
Proximate analysis (wt%)							
Volatiles	–	–	7.3	0.67	2.9	1.2	–
Fixed carbon	–	–	B.d.	90.8	B.d.	B.d.	–
Ash	–	< 12	20.1	8.41	14.3	16.5	–
Moisture	–	–	14	0.09	0.9	1.0	–
Textural characteristics							
SBET (m^2/g)	–	51	60	60	–	–	61
Total pore volume (cm^3/g)	–	–	–	–	–	–	0.28
Average pore size (nm)	–	23	–	–	–	–	–
Reference	[115]	[49]	[4]	[111]	[31]	[64]	[34]

Pyrolysis reactor type	Pilot distillation unit	Horizontal tubular	Horizontal furnace (550 °C)	Horizontal furnace (800 °C)	Muffle furnace (500 °C)	Muffle furnace (600 °C)	Static-bed under vacuum	Fluidized bed*
Ultimate analysis (wt%)								
C	86.3	–	83	78.5	81.24	81.26	85.18	90.5 ± 1.13
H	0.3	–	1.4	0.5	2.02	1.76	1.15	2.5 ± 0.1
N	0.3	–	0.4	0.3	0.24	0.24	0.639	0.3 ± 0.04
S	2.8	–	1.7	2.4	1.67	2.33	2.03	–
Proximate analysis (wt%)								
Volatiles	1.8	0.41 ± 0.2	–	–	–	–	–	–
Fixed carbon	91.3	90.5 ± 11.8	–	–	–	–	–	–
Ash	12.5	8.63 ± 0.45	6.5	4.4	5.87	4.15	13.24	7.7 ± 0.8
Moisture	0.4	0.46 ± 0.02	–	–	–	–	–	–
Textural characteristics								
SBET (m^2/g)	64	72	32	100	156	136	–	175.4 ± 20.11
Total pore volume (cm^3/g)	0.4	–	0.274	0.738	0.123	0.193	–	–
Average pore size (nm)	–	–	8.7	7	–	–	–	–
Reference	[36]	[37]	[38]	[38]	[39]	[39]	[42]	[116]

* Fast pyrolysis of pitch pine for 2 s at 500 °C using a fluidized-bed reactor under oxygen-free conditions.

from ELTs are significantly lower than those originated from biomass.

4.6. Material and energy balances of pyrolysis process

Typical material balances for the pyrolysis of waste tyres, based on a custom feed rate of each industrial plant are presented on Table 3. These data represent steady state conditions and are also in agreement with other published results [117]. Depending on feedstock characteristics, reactor type and pyrolysis conditions, the product yields could be distinctively reported. In total, the product yields (steel free, aprox. 15% steel) can be categorised: Gas yield: 9–25 wt%; Liquid yield: 33–47 wt%; Char yield: 28–33 wt%.

The products from 1 t of EL Tyres rotary kiln pyrolysis are the following: 440 kg of oil, 300 kg of carbonised products and 150 kg of steel [117].

The balances provide additional insight into the material flows that might be anticipated from any ELTs pyrolysis project.

Pyrolysis of ELTs is an endothermic reaction. Its final calorific value depends on temperature, heating rate, residence time in final temperature. These parameters affect product yields along with their calorific value. However, ELTs pyrolysis calorific value is between 2 MJ/kg and 4 MJ/kg [63,96].

4.7. Pyrolysis mechanism and kinetics

Research on pyrolysis mechanism and kinetics is very important not only for proper reactor design but also for obtaining a desired product profile. When tyre particles heat in a pyrolysis reactor, pyrolysis occurs as a certain temperature is reached on the particle's surface. There are two stages detected in pyrolysis: primary pyrolysis and secondary cracking. The vapor or volatiles produced firstly from end of life tyres is made up of a wide variety of hydrocarbons and then could be implicated to secondary reactions.

The pyrolysis kinetics should include the exothermic tyre pyrolysis reactions but also the endothermic evaporation of the pyrolysis products. As for the thermal decomposition of organic polymers, four general mechanisms can be identified: (1) random chain scission; (2) end chain scission; (3) chain stripping; and (4) cross-linking [118].

Wey et al. [118] showed that pyrolysis is strongly influenced by the following parameters: temperature, retention time of the volatiles at the reaction zone, and pressure and type of gaseous atmosphere. Cracking occurs at higher temperatures and enables primary products to be converted into compounds which may have a higher market value. One method is the aromatization of products generated by primary pyrolysis. Pyrolysis produces maximum yields of aromatic components at temperatures between 700 °C and 800 °C. Fuel oil is produced without much gas at low temperature (below 500 °C) and the char fraction was found to decrease as temperature increases from 300 °C to 720 °C.

Pyrolysis kinetics of the scrap tyre rubbers can be well represented by the first-order irreversible decomposition reactions of its components [45]. Typical curves of derivative thermogravimetry (DTG) and thermogravimetric analysis (TGA) provide valuable information on pyrolysis kinetics and mechanisms of scrap tyre rubbers.

Thermogravimetric analyser (TGA) is used in order to study tyres conversion and kinetics and estimate the temperature of product release. Many researchers have been working on TGA: Chen et al. [119], used a thermogravimetric system (Shimadzu TGA-50). Islam et al. [120], used tyre samples of 9 mesh (or 2 mm) at a Pyris Diamond Thermogravimetric/Differential Thermal Analyzer (TG/DTA) and differential-thermogravimetric (DTG). The samples' weight was about (15–20 mg) in a temperature range of 30–800 °C under steady nitrogen flow at 100 ml/min. Williams et al. [22], pyrolysed 3 ELT samples in a TGA apparatus under nitrogen atmosphere with a heating rate that varies from 5 K/min to 80 K/min while De Marco Rodriguez [50], used temperatures 300–700 °C in a thermogravimetric analyser. Murillo et al. [111], used a SETARAM TG DTA-92 TGA device controlled by PID temperature controller. Nitrogen was used for pyrolysis with a heating rate of 20 °C/min and final temperature from 400 °C to 600 °C. The conversion obtained for the scrap tyre pyrolysis is always close to the maximum possible above 500 °C and the oil yields were always higher than 40%. No influence of the reaction time and heating rate on the total conversion and oils yield has been observed in the temperature range studied.

Kinetic modeling of tyre pyrolysis is based mainly on data from TGA or DTG where model equations are used to deconvolute the peaks in the thermograms.

Most pyrolysis models assume a kinetic rate-limiting type of reaction and do not consider heat or mass transfer limitations in a reactor [121]. All kinetic data in order to be processed, three assumptions should be fulfilled; (1) Major components in the tyre (processing oils, polyisoprene, polybutadiene, styrene–butadiene copolymer) thermally decompose independently without any interaction among them; (2) The decomposition reactions are

Table 9
Literature tyre pyrolysis kinetic data.

Tyre sample	Reaction order	Pre-exponential factor A (min^{-1})	Activation energy E (kJ/mol)	Reference
Shredded tyre (TGA)	1.62	2.06×10^{10}	1322	[136]
Car tyre	1.98	7.57×10^{10}	148	[135]
Truck tyre	1.63	5.05×10^{10}	148	[135]
Natural rubber	1	3.89×10^{16}	207	[137]
Butadiene rubber	1	6.32×10^{14}	215	[137]
Styrene butadiene rubber	0.9–1.2	4.3×10^{13}–4.7×10^{10}	238–241	[138]
Shredded tyre	1	441×10^{4}	98.6	[72]
Used Tyres (fast pyrolysis)	1	97.8	65.6	[139]
Tyre powder	1	1.03×10^{23}	229.58	[140]
Natural rubber	1	3.27×10^{9}	126.7 ± 11.7	[45]
Styrene butadiene rubber	1	1.31×10^{14}	201.1 ± 13.9	[45]
Tyre partcles (one stage model)	0.894	1.82×10^{5}	78.62	[126]
Tyre partcles (two stage model)				
1st stage	1	2.32×10^{5}	79.86	[126]
2nd stage	1	94.8×10^{5}	128.44	[126]
NR (nonlinear)	1.32 ± 0.08	$(79.2\pm3)\times10^{11}$	150 ± 20	[127]
SBR (nonlinear)	1.7 ± 0.2	$(108\pm12)\times1010^{14}$	200 ± 20	[127]
BR (nonlinear)	1.1 ± 0.08	$(64.8\pm3)\times10^{7}$	125 ± 6	[127]

irreversible in an only one mechanism; (3) Data from DTG curves were necessary to estimate the initial tire composition, the devolatilization rate of every component, plus its kinetic parameters [122].

The general tyre pyrolysis reaction could be written as:

$$r = kC^n \tag{1}$$

A common method in modeling pyrolytic reactions is to utilize Arrhenius type equations, where the rate constant is of the form:

$$k = Ae^{-\frac{E_a}{RT}}. \tag{2}$$

This gives the classic pyrolysis model as a function of both temperature and reactant mass concentration:

$$r = Ae^{-\frac{E_a}{RT}}C^n \tag{3}$$

In this case, C may be substituted with the normalized mass fraction of the tire sample that has decomposed, X, as measured in the TGA:

$$X = \frac{m_0 - m}{m_0 - m_\infty} \tag{4}$$

Therefore, the rate of reaction, r, would be rate of mass loss of the tire sample. For isothermal conditions, the rate of mass loss with respect to time can be written as:

$$\frac{dX}{dT} = Ae^{-\frac{E_a}{RT}}(1-X)^n \tag{5}$$

For non-isothermal pyrolysis conditions where the heating rate is constant, i.e., $dT/dt = \boldsymbol{\beta}$, such that:

$$\frac{dX}{dT} = \frac{1}{\beta}Ae^{-\frac{E_a}{RT}}(1-X)^n \tag{6}$$

A linearized form of the differential Eq. (5) gives:

$$\ln\left(\frac{dx}{dt}\right) = \ln A - \frac{E_a}{RT} + \ln(1-X)^n \tag{7}$$

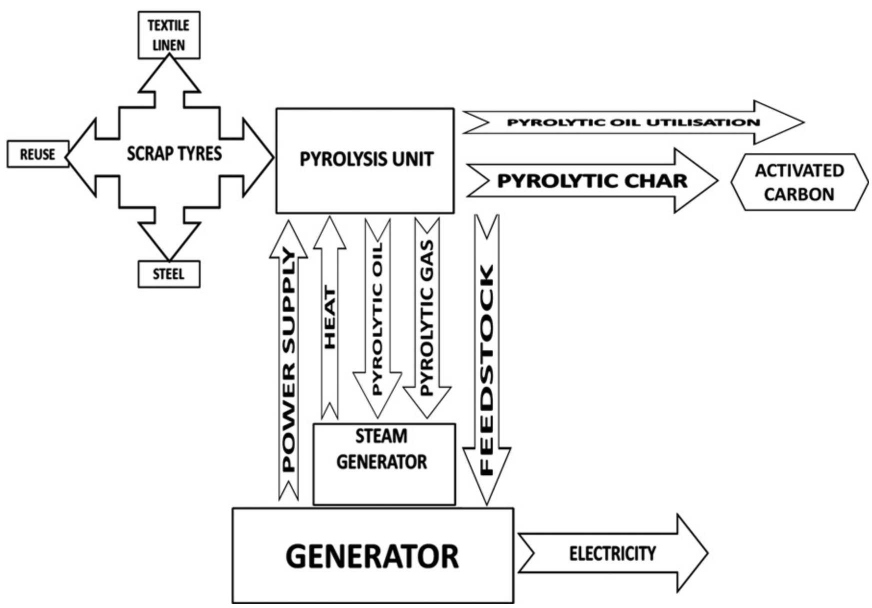


Fig. 1. Tyre pyrolysis flowsheet.

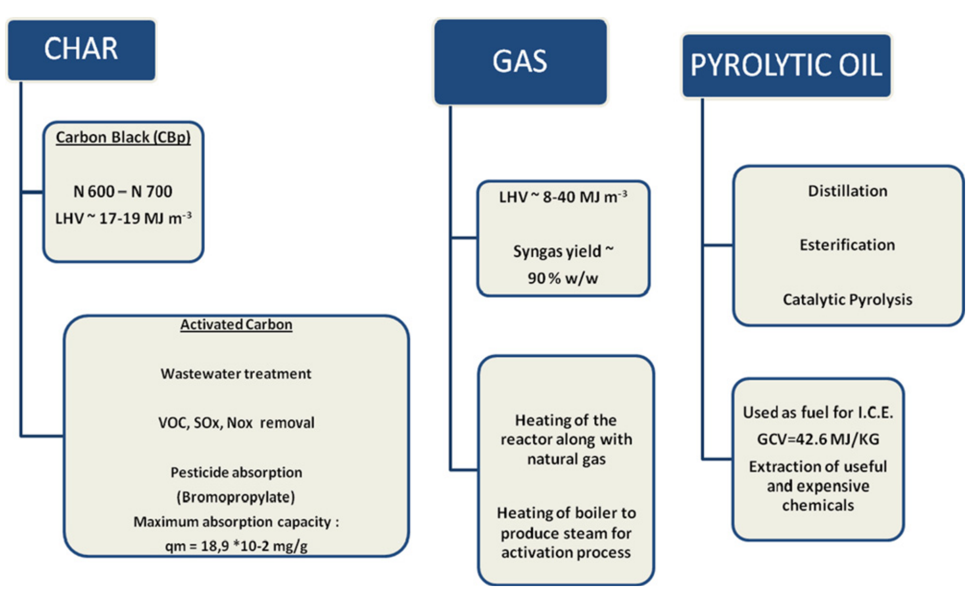


Fig. 2. Uses of tyres pyrolysis products.

In the case of first order reaction ($n=1$), the values of $\ln[(dx/dt)/(1-X)]$ are plotted against $-1/T$ and the values of E_a and A can be obtained from the gradient and y-intercept, respectively. Similarly, Eq. (6) can be linearly expressed as:

$$\ln\left(\frac{dx}{dt}\right) = \ln\frac{A}{B} - \frac{E_a}{RT} + n\ln(1-X) \quad (8)$$

However, if an integral approach is used; integrating Eq. (6) yields the following equations:

$$\text{For } n=1\ \ln(1-X) = \frac{A}{\beta}\int e^{-\frac{E_a}{RT}}dT \quad (9)$$

$$\text{For } n \neq 1\ \frac{(1-X)^{1-n}}{n-1} = \frac{A}{\beta}\int e^{-\frac{E_a}{RT}}dT \quad (10)$$

There is no exact analytical solution to the integrals in Eqs. (9) and (10), so approximations are often used. The most commonly used approximation expansion is the one developed by Coats and Redfern [123] or Runge–Kutta algorithm etc.

Bouvier et al. [124] found that rubber degradation is an one-step mechanism and proposed to be a first-order reaction. Senneca et al. [125] investigated that the primary and secondary pyrolysis stages take place at small heating rates (5–100 K/min). At large heating rates (900 K/min), however, the phenomenon is no longer observed and only a single peak exists in the pyrolysis rate. Many authors have proposed sets of formal kinetic parameters for the different rubber types. These studies were mainly performed with microbalance in which only small samples with fine particle materials were investigated. However, the pyrolysis behaviour of large tyre particle samples may be closer to the exact pyrolysis process. The findings on tyre, and/or its constituents, pyrolysis kinetics based on literature search, are presented on Table 9.

5. Sustainability of tyres pyrolysis

5.1. Pyrolysis feasibility and product uses

Pyrolysis of ELT can produce a wide range of useful products (Figs. 1 and 2). The gases are useful as fuel due to their high values of LHV (>40 MJ/N m^3). They can sufficiently cover needs of the pyrolysis plant apart from start up period. Pyrolytic gas can be used as a sole fuel or it can be mixed with natural gas or propane in a pre-determined ratio.

The derived oils may be used directly as liquid fuels or added to petroleum refinery feedstocks. They may also be an important source of refined chemicals [128]. Murugan et al. [129], concluded that the modification of the crude tyre pyrolysis oil involves three stages, (i) moisture removal (ii) desulphurisation and (iii) vacuum distillation.

The solid char may be used either as a smokeless fuel, carbon black or activated carbon or can be gasified for the production of fuel gases. Activated carbon is a widely used adsorbent with a large field of applications including: (a) water purification (dissolved organics and toxic compounds, dechlorization, die removal, municipal drinking water treatment, swimming pools, etc.), (b) air purification (volatile inorganic and organic removal, solvent recovery, gas desulfurization, etc.), (c) batteries, fuel cells, nuclear power station, and (d) others, such as cigarette filters and food industry [130].

Tyre char air reactivity is dependent on pyrolysis temperature. Tyre chars present higher reactivities with steam than with CO_2 and show surface areas comparable to commercially available active carbons (areas around 1100 m^2/g) [21]. Activated carbons can be produced by physical or chemical activation. The KOH activation process seems to be the preferable one, due to the high adsorption capacities of the products [130,131].

Pyrolysis of scrap tyres has not been commercially successful mainly because of the poor quality of the heterogeneous nature of the carbon rich pyrolysed by-product. A thorough look for practical methods to post-treat the pyro-carbon into market is necessary. CBp Carbon Industries Inc products were selected and claimed as the "best-available- technology" since they successfully fulfill European Union Cooperative Research (CRAFT) Recycle Tire contract GIST-CT-2002-50281. The received crude pyro-carbon if refined and upgraded, can give functional grades of reinforcing black fillers such as CBpEX, CBpES and CBpEU which can be substituted and blended with *N*-500, *N*-600, *N*-700 and *N*-900 series of standard commercial carbon black grades. The significance of this recognition of the patented CBp Carbon nano-carbon production technology break through, is that there is now a new large market potential for remanufacturing products from scrap tyres. Plans are being made for additional CBp Carbon plants in Europe, North America and Australia [132].

5.2. Economic viability

Currently, the widely used methods of recycling all over Europe, face problems identified in the commercialization and profit generation. Major amount of tyres end up to further use in a form of rubber crumb, but only minor recyclers offer full, ecologically safe processing of tyres (via pyrolysis, thermolysis, etc). Economic viability remains the major issue.

The research on economically profitable ways of pyrolysis and other methods of recycling, might be able to evolve rubber-waste utilization, from the current position of being burden to producers, to profitable enterprises. It is not only making Europe greener via utilizing wastes, but creating also a considerable amount of jobs. This could be a solution for a further development of utilization and recycling automotive tyres in different regions of the European Union into profitable enterprises rather than, obligatory burden on producers.

Understanding the cost-effectiveness and the role of economic and policy instruments, such as the combined tax-recycling subsidy scheme for ELTs recycling, it is proven to be of crucial importance in a market-oriented environmental management system. At the moment, there is an important niche market in relation to this kind of technology. In countries such as USA, Canada, Japan and most European Countries the success of pyrolysis is mainly based on the polluter's responsibility system. All of these systems are economically characterised, depending on the market of the pyrolysis materials. As for industrial applications and further valorisation of tyres, materials' production is the key factor.

The market for ELTs treatment is a long-term growing market. The number of pyrolysis plants has increased the last decade. The European Union Policy and financing, has played a key role in putting the experimental practice into the market. A CBp Carbon plant in Hungary, which is presently being scaled up for increased capacity, accredited tests that were approved by EU for tyre recycling [132]. Another plant is planned to recycle 100 t per day or 30,000 t of scrap tyres per year. This will produce an additional 10,000 t of CBp functional black reinforcing filler, a very small quantity considering the large carbon black market potentials [132]. Nowadays, pyrolysis plants have been constructed in some countries in Europe (e.g., Cyprus) for carbon black production.

There is a number of factors which would seem to be favoring an increased use of tyres pyrolysis facilities. The decision for a tyre depolymerisation plant for a waste management company, in order to produce energy and materials, will depend on whether

the costs of the pyrolysis process are less than that of incineration or thermal treatment. A tyre pyrolysis plant is a profitable investment but strongly dependent on various factors; product price, production capacity, total production cost, capital investment and the tipping fee.

Another factor which may influence the decision-making process, is the selection method of tyres, of the country concerned. A non collected and dispersed system may characterize an investment in smaller-scale facilities prohibitive. Large capacity production units will be required to give attractive economics and this may pose problems in small markets.

Tyre pyrolysis plant's economics are very sensitive in product yield, since economics are substantially affected by the selling price of the solid product, which is based on its quality (adsorption capacity) and not on weight. Today's challenge is, to specifically choose the type of product of the industrial pyrolysis plant and its desired properties in a sustainable and eco-friendly frame that reuses or diminishes any harmful by-products. Additionally, production of high value chemicals is possible, thus enhancing company's profit.

Last but not least cost-affecting factors, are the raw material cost (low cost or even better free of charge) and plant capacity. The report "End of life tyres", published in 2010, European Tyre & Rubber Manufacturers Association (ETRMA) states that "the economic viability of this alternative route for high temperature resource recovery from tyres is hampered by the fact that the prices obtained for the by-products often fail to justify the process costs. Under current market conditions the economic viability of these options has yet to be proved (there are few or no large-scale plants currently in operation) but they have the merit to offer scope for increasing recycling rates" [133].

5.3. *Energy requirements*

Pyrolysis process is considered to be a process characterised by excess of energy. In order to maintain a sustainable profile for a pyrolysis plant, tyre-derived gas or tyre derived fuel can be used, providing sufficient heat to cover energy needs. Alternatively, the use of supplemental fuel – propane or natural gas – can be promoted, especially for start up period. The electricity needs of a pyrolysis system are estimated to range between 12.8 and 117.6 kW h/t feedstock plus the heat required to sustain the pyrolysis reaction (approximately 406–662 kW h/t) of feedstock) [134].

5.4. *Environmental sustainability*

The energy and material recovery from tyres has experienced a significant increment the last decade due to the stringent EU and National Directives, comparing to tyres management. In the situation described above, it is clear that the new targeted pyrolysis technology would easily take an important share of the market of tyres management, only limited by environmental laws, where in some countries pyrolysis is characterised as incineration.

Pyrolysis is an environmentally safe process. The produced pyrolytic gas can be used alternatively to replace up to an extent, natural gas or propane, in simple appliances, providing energy/heat where needed. This could be proved a very interesting route for pyrolytic gas utilisation, saving at the same time an appreciable quantity of natural gas.

The reusable char can be improved to CBp Carbon. The CBp carbon products are physically recovered from the scrap tyres instead of combustion. Every pyrolysis to carbon black plant can reduce or conserve approximately 40,000 t of carbon dioxide greenhouse gas emissions that are released to the atmosphere by the current methods of burning oil or gas feedstocks for production of the equivalent amount of commercial carbon blacks [132]. Furthermore, soil contamination can be decreased since less landfills would receive ELTs. Finally, pyrolysis can produce considerable amounts of energy, thus preserving than using at the same time, food resources. The use of recycled carbon black, can prevent the production of a minimum of 5 t of CO_2 emissions (the production of a single tonne of virgin carbon black). Pyrolysis is a method of recovering the maximum value from tires (e.g., materials and energy) and thus helps in preservation of fossil fuels and minerals.

Furthermore, activated carbon production from ELTs pyrolysis can be characterised as a route toward environmental sustainability. Zabaniotou et al.[4,24] proved that the production of activated carbons is viable, while at the same time it does not consume significant amount of resources. The received product displayed similar characteristics to NORIT GL-50 and can be used in environmental friendly appliances such as the removal of dangerous pesticides from urban waters or as filter in gas cleaning appliances.

More specifically, carbonaceous adsorbents are developed from ELTs and tested as adsorbents of Cd^{2+} in aqueous solutions, methoxychlor, atrazine and methyl parathion in waste water and also copper and *p*-nitrophenol and *p*-chlorophenol in aqueous solutions [141,142,37,143].

The liquid product, tire-derived oil, is condensed and cooled. Light and heavy oil fractions may be handled separately. Pyrolytic oil may contain polyaromatic hydrocarbons (PAH) [29]. Pyrolytic oil, if treated, can be used as a liquid fuel (GCV ~42 MJ/kg) or as a precursor for valuable chemicals. This treatment involves hydrogenation, desulphurisation and as a result the received oil can be used as fuel since it has characteristics that do not violate strict environmental regulations [117]. The oil can also be distilled into different fractions: a light, a middle distillate and a heavy fraction. If subjected to fractional distillation, the oil would reportedly yield a gasoline fraction (Table 7). The light fraction was positively tested as a gasoline additive. Furthermore, this fraction contains valuable chemicals such as D,L-limonene. The middle fraction was successfully tested as a plasticizer in rubbers. The heavy fraction represents a good-quality feedstock for the production of coke and can also be used in road pavements.

6. Conclusions

The study showed the following technical features:

- Attending the advances in pyrolysis applications, laboratory and bench scale pyrolysis of end of life tyres have been studied thoroughly, while pilot/demonstration or industrial applications are relatively few.
- Several types of laboratory scale pyrolysis of end of life tyres (ELT) have been tested by many researchers either by the use of catalyst or not. More specifically, fixed bed, rotary kiln and fluidized bed reactors were used to determine the basic characteristics of pyrolysis procedure under typical pyrolysis conditions ($400\ ^\circ C < T$ operation $< 600\ ^\circ C$, 0.5 min $< T < 120$ min, inert atmosphere).
- Innovating pyrolysis types such as flash, plasma and molten salt type were investigated by few researchers. These processes are characterised by heating rate $> 1000\ ^\circ C/s$, final pyrolysis temperature $> 1500\ ^\circ C$ and high heat transfer/reaction medium, respectively.
- Kinetic studies were mostly based on TGA experiments and in most of the cases a 1st order reaction fitted the process, with values for pre-exponential factor in the range of $A = 10^{10}$–10^{16} min and activation energy ranging from $E = 100$–250kJ/mol.

- Pilot units operated so far, are mainly based on batch rotary kiln reactors and aimed at the production of both energy and carbon materials. The operation conditions reported are, for temperature ranging from 400 °C to 600 °C and under atmospheric pressure.
- By pyrolysis, the rubber portion of used tires is transformed into gas, oil and char.
- Pyrolytic gas can be used, if cleaned, as a gas fuel due to its high LHV (36–51 MJ/N m^3). The pyrolytic gas can be also used as a make-up heat source for the pyrolysis process.
- Pyrolytic oil, if treated, can be used as a liquid fuel (GCV ~ 42 MJ/kg) or as a precursor for valuable chemicals.
- The use of untreated pyrolytic oil in burners might create environmental problems due to its sulphur content.
- Pyrolysis char can be used either as a fuel or as carbon black filler. Pyrolytic char has a low adsorbing capacity ($60\ m^2/g < S_{BET} < 82\ m^2/g$). However, after activation, the char's adsorbing capacity can be increased significantly ($S_{BET} > 600\ m^2/g$).
- Pyrolysis CBs surface chemistry and activity is similar to those of commercial carbon blacks (*N*-351, *N*-650).

The study has also concluded in some sustainability and policy features, the following:

- Tyres cover a wide range of materials which can be recovered (steel, fibers, shredders, energy, oils, carbon filer, activated carbon etc). Pyrolysis offers an efficient route for high temperature resource recovery from tyres.
- Although pyrolysis could play a very important role in "new generation" biofuels and resources conservation, it faces limitations due to the fact that it is still classified as incineration by legislation.
- The cost and operation of an ELT pyrolysis plant depends on various factors such as the production capacity, production cost, capital investment, product price and last but not least, the tipping fee which is applied is some European countries. Nevertheless, the properties of the end products from ELT pyrolysis and especially of char, affect the thermal processes' economic balance. The valorisation of char for active carbon production or high added value material (carbon filter), positively affects the economics of pyrolysis.
- Pyrolysis applications, with competitive cost and significant income from products selling, provide evidence of large possibilities for small and medium enterprises in every country. However, the development of an efficient, eco-friendly and cost effective pyrolysis plant with marketable products is the most essential feature. Extensive testing of the technology, materials, products and processes prior to their presentation in the market are necessary for a sustainable and trustworthy alternative with multiple benefits to environment and local communities.

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